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Characterization of oligomers from methylglyoxal under dark conditions: a pathway to produce secondary organic aerosol through cloud processing during nighttime

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Abstract. Aqueous-phase oligomer formation from methylglyoxal, a major atmospheric photooxidation product, has been investigated in a simulated cloud matrix under dark conditions. The aim of this study was to explore an additional pathway producing secondary organic aerosol (SOA) through cloud processes without participation of photochemistry during nighttime. Indeed, atmospheric models still underestimate SOA formation, as field measurements have revealed more SOA than predicted. Soluble oligomers ($n = 1$–8) formed in the course of acid-catalyzed aldol condensation and acid-catalyzed hydration followed by acetal formation have been detected and characterized by positive and negative ion electrospray ionization mass spectrometry. Aldol condensation proved to be a favorable mechanism under simulated cloud conditions, while hydration/acetal formation was found to strongly depend on the pH of the system and only occurred at a pH$<$3.5. No evidence was found for formation of organosulfates. The aldol oligomer series starts with a β-hydroxy ketone via aldol condensation, where oligomers are formed by multiple additions of $C_3H_4O_2$ units (72 Da) to the parent β-hydroxy ketone. Ion trap mass spectrometry experiments were performed to structurally characterize the major oligomer species. A mechanistic pathway for the growth of oligomers under cloud conditions and in the absence of UV-light and OH radicals, which could substantially enhance in-cloud SOA yields, is proposed here for the first time.

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1 Introduction

Secondary organic aerosol (SOA) is a substantial component of total organic particulate matter but little is known about the composition of SOA formed through cloud processing. It has been proposed that, like sulfate, SOA can form through cloud processing, where the high hydroxyl radical concentration in the interstitial spaces of clouds can lead to oxidation of reactive organic molecules to form highly water-soluble compounds such as aldehydes (Blando and Turpin, 2000; Ervens et al., 2004; Lim et al., 2005). In-cloud SOA production from alkenes and aldehydes, including isoprene, has been modelled by Lim et al. (2005), where gas-phase isoprene oxidation produces water-soluble compounds including glycolaldehyde, glyoxal, and methylglyoxal. The partition of the latter products into cloud droplets depends on their reactive uptake coefficients, and, after uptake in the aqueous phase, they can undergo diverse chemical reactions leading to heavier and less volatile molecules. Upon evaporation of

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the cloud droplets the low-volatile organics will remain in part in the particle phase, yielding SOA.

Methylglyoxal is found widely in urban, rural, and remote environments (Kawamura et al., 1996; Kawamura and Yasui, 2005). It is produced in high yield from the oxidation of biogenic volatile organic compounds (VOCs) (e.g., isoprene) (Smith et al., 1999; Atkinson and Arey, 2003; Ham et al., 2006) and anthropogenic VOCs (e.g., mono- and polycyclic aromatics: "BTEX" = benzene, toluene, ethylbenzene, xylenes) (Atkinson, 2000; Atkinson and Arey, 2003). Fu et al. (2008) have constructed a global budget of atmospheric glyoxal and methylglyoxal with the goal of quantifying their potential for global SOA formation via irreversible uptake by aqueous aerosols and clouds. An annual global production of 140 Tg of methylglyoxal has been estimated, with biogenic isoprene being the major precursor contributing 79%, and acetone (mostly biogenic) being the second most important one.

Irreversible heterogeneous uptake of dicarbonyls in clouds or aerosols (probably due to various oligomerization processes) has been suggested as a significant source of SOA, such as, for example, for glyoxal (Volkamer et al., 2007) and both glyoxal and methylglyoxal (Fu et al., 2008). Different aqueous-phase chemical processes have been proposed which could lead to irreversible uptake of methylglyoxal by aqueous aerosols and cloud droplets:

- The first process involves oxidation to produce non-volatile organic acids such as glyoxylic, pyruvic, and oxalic acid (Crahan et al., 2004; Ervens et al., 2004; Warneck, 2005; Sorooshian et al., 2006, 2007).
- The second process concerns oligomerization of dicarbonyls essentially via hydration and acetal reactions (Schweitzer et al., 1998; Kalberer et al., 2004; Hastings et al., 2005; Liggio et al., 2005a, b; Loeffler et al., 2006; Zhao et al., 2006).
- The third process involves photooxidation of dicarbonyls, including (a) aqueous-phase oxidation of dicarbonyls to organic acids which oligomerize via esterification (Altieri et al., 2006, 2008); and (b) condensed-phase oligomerization (Guzman et al., 2006).
- The fourth process relates to ammonium-catalyzed aldol condensation as an important sink for carbonyl compounds in tropospheric aerosol formation (Galloway et al., 2009; Nozière et al., 2009; Shapiro et al., 2009; Sareen et al., 2010).

These four processes have the potential to account for the high oligomer and organic acid concentrations detected in ambient aerosols (Carlton et al., 2007; Denkenberger et al., 2007).

Methylglyoxal is an important intermediate in in-cloud reactions of many reactive organic compounds. The atmospheric lifetime of methylglyoxal is estimated at $\sim$1.6 h, against photolysis and oxidation by the OH radical (Fu et al., 2008); however, methylglyoxal can also be taken up by aqueous aerosols and cloud droplets on account of its high water-solubility. Methylglyoxal has been found at significant concentrations in ambient aerosol, for example, in urban total aerosol from Tokyo, Japan, the concentrations of methylglyoxal were in the range 4.7–52 ng m^{-3} (Kawamura and Yasui, 2005), suggesting that mechanisms exist for introducing methylglyoxal into the aerosol phase. To ascertain the fate of methylglyoxal in view of its short life-time in the atmosphere, dark chamber experiments have been carried out under simulated cloud conditions. The present work focuses on the mechanistic and structural elucidation of oligomers formed in the aqueous phase under these conditions.

2 Experimental

2.1 Sample preparation

Methylglyoxal (MGly) solutions were prepared using commercial 40 wt% methylglyoxal in water (Fisher Scientific) and ultrapure water (Millipore ultrapure water system, maximum resistivity 18 MΩ.cm). Experiments were carried out in a 175 mL thermostatted (14–15 °C) and light-protected cell (electrochemistry reaction cell). With the goal of simulating the cloud conditions in a bulk system, different concentrations (10^{-4} to 10^{-5} mol L^{-1}) of inorganic salts ($(NH_4)_2SO_4$, Na_2SO_4) and H_2SO_4 (10^{-6} mol L^{-1}) were added with a syringe to a continuously stirred solution of MGly (10^{-3} mol L^{-1}). A limited range of acidic conditions (pH = 3–5) and ionic strengths was produced and analyzed.

2.2 Electrospray-mass spectrometry (ESI-MS)

Samples were taken every 20-30 min from the reaction cell, diluted [1:1 (v/v) ratio] with methanol (or acetonitrile or acetone), and the pH of the final solution was monitored with a micro pH meter. Then, these solutions were introduced into a classic (LCQ) quadrupole ion trap (Thermo Scientific, San Jose, CA, USA) equipped with an electrospray source. First-order spectra were acquired in the range m/z 50-1000 in both the positive and negative ion mode. The electrospray source and ion trap were operated under the following conditions: flow rate, 5 µL min^{-1}, electrospray ionization voltage, 4.5–5 kV in the positive mode and 3 kV in the negative mode; capillary temperature, 125 °C; drying and nebulizer gas, nitrogen; and maximum ion injection time, 200 ms.

The ESI-MS technique uses a soft ionization process that does not fragment compounds and provides molecular weight information with unit mass resolution. The LCQ ion trap mass spectrometer was also used to obtain structural information for a selected number of ions. To achieve fragmentation, a selected ion is collided with the buffer gas (helium) of the ion trap, and fragments are analyzed (MS/MS or MS^2; MS^3 if the process is repeated on product ions of MS^2). For

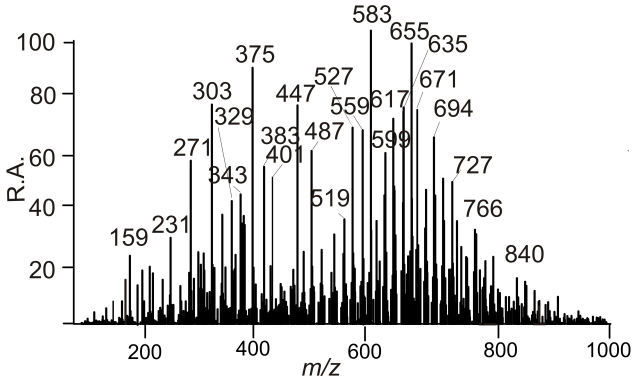


Fig. 1. ESI mass spectrum (positive mode) obtained from the reaction mixture of MGly (10^{-3} mol L^{-1}) with ammonium sulfate (10^{-4} mol L^{-1}) at pH = 4.5 and T = 15 °C after one hour reaction.

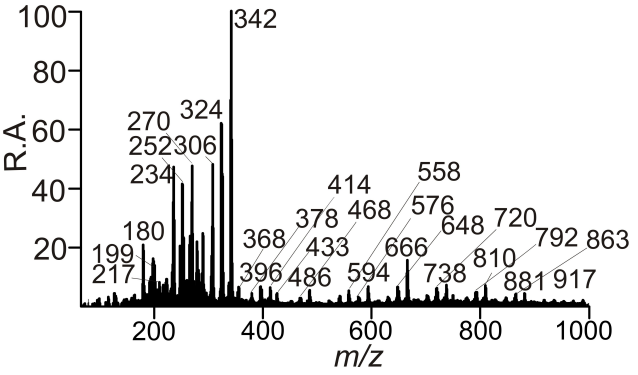


Fig. 2. ESI mass spectrum (positive mode) obtained from the reaction mixture of MGly (10^{-3} mol L^{-1}) with ammonium sulfate (10^{-4} mol L^{-1}) at pH = 3.2 and T = 15 °C after one hour reaction.

MS^2 and MS^3 experiments, an isolation width of 2 m/z units and a normalized collision energy level of 35% were applied.

3 Results and discussion

3.1 Mass spectral results

In the present work, only mass spectral data obtained upon dilution of reaction products with methanol are discussed; methanol was selected because it is the most commonly used electrospray solvent and results in a stable spray (Nemes et al., 2007). It is also well documented that a significant amount of methanol is present in cloud water (Leriche et al., 2000; Laj et al., 2009). Hence, it is possible that if oligomers containing free aldehyde groups are formed in the atmosphere, they can react with methanol and can produce acetals and hemiacetals. However, it is more likely that under natural cloud conditions the hydrates of aldehyde-containing oligomers will prevail.

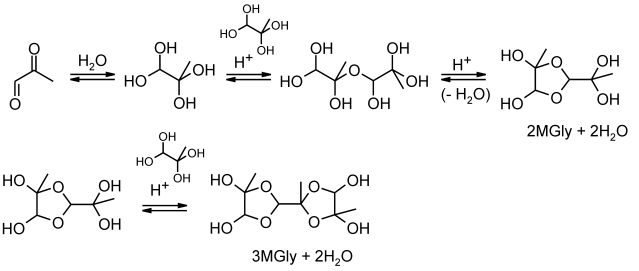
After one hour in the simulated cloud medium, the first-order mass spectra of the MGly reaction mixture revealed a complex composition with m/z values between 200 and 800 (Figs. 1 and 2). Information on control experiments (Table S1, http://www.atmos-chem-phys.net/10/3803/2010/acp-10-3803-2010-supplement.pdf) and resulting first-order mass spectra (Figs. S1–S8, http://www.atmos-chem-phys.net/10/3803/2010/acp-10-3803-2010-supplement.pdf) for comparison are provided in the supplement. The mass spectra showed an increasing complexity with reaction time and regular patterns of mass differences (12, 14, and 16 units), suggesting the presence of several oligomer series with overlapping peaks (Limbeck et al., 2003; Kalberer et al., 2004; Tolocka et al., 2004). Moreover, adducts with alkali metal ions (i.e., Na^+, K^+), the chloride ion (Cl^-) and methanol could be formed upon electrospray ionization, further complicating structural interpretation. Nevertheless, higher-molecular weight (MW) compounds are produced from MGly at relatively low concentrations in a simulated cloud medium without photochemical action. This chemical process occurs quickly as the abundance of ions with higher m/z ratios considerably increases within an hour and strongly depends on the initial MGly concentration, acidity, and ionic strength (NH_4^+, Na^+, SO_4^{2-}). It has been reported that the NH_4^+ ion can catalyze oligomerization reactions (Nozière et al., 2009; Sareen et al., 2010); however, oligomerization was found not only to depend on the NH_4^+ ion concentration but rather to be affected by the cation ionic strength and the acidity of the medium. In the present study, only results relevant to cloud conditions are discussed. In order to simulate natural conditions, ammonium sulfate was chosen because it encompasses 60–70% of total inorganic salts in the troposphere (Falkovich et al., 2005; Rincon et al., 2010). By increasing the concentration of MGly, to simulate the evaporation of a cloud droplet with a typical lifetime of 10 min (De Haan et al., 2009), the production of higher-MW compounds was found to be quasi instantaneous.

3.2 Potential oligomerization mechanisms

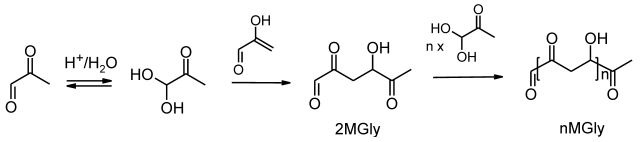
In order to characterize the numerous ions observed in the ESI mass spectra, it is relevant to understand which type of reactions and products are possible when reacting methylglyoxal in slightly acidic medium at low temperature and low concentrations of inorganic salts such as encountered in natural cloud conditions.

3.2.1 Hydration/acetal formation followed by acid-catalyzed oligomerization

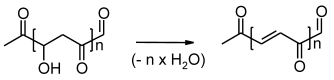
Several studies dealing with the self-oligomerization of glyoxal provide evidence for hydration followed by acetal/hemiacetal formation (Kalberer et al., 2004; Hastings et al, 2005; Liggio et al., 2005a). This self-oligomerization could lead to different molecular structures; however, it has been shown that the dominant oligomer formed via this



Scheme 1. Potential mechanism for hydration/acetal formation from aqueous MGly solutions.



Scheme 2. Potential mechanism for formation of aldol condensation products from aqueous MGly solutions.



Scheme 3. Potential mechanism for dehydration of aldol condensation products leading to SOA during cloud evaporation.

mechanism are five-membered ring systems with intervening single bonds. Indeed, these structures are stable owing to the free rotation of the central C–C bond when compared to other rigid six-membered ring structures. This mechanism, first established for glyoxal, likely operates for methylglyoxal in acidic medium, as proposed by Zhao et al. (2006) and shown in Scheme 1.

3.2.2 Acid-catalyzed aldol condensation

A key structural feature of MGly is its methyl ketone function. Indeed, the keto form is in equilibrium with the enol form in aqueous media by tautomerization. In addition, the enol form of MGly is stabilized in acidic medium through conjugation with the second carbonyl group. MGly can therefore undergo aldol condensation as proposed in Scheme 2, where oligomerization proceeds by the successive addition of a β-hydroxy ketone unit. We observed that this type of accretion reaction does occur at higher pH values than hydration/acetal formation (first mechanism) and therefore could be favored in a cloud medium. If these aldol oligomers are formed in a cloud droplet, they will have a sufficiently low volatility to produce new SOA upon droplet evaporation. Further dehydration of these compounds could take place via crotonization, leading to highly conjugated molecules (Scheme 3). The UV-visible absorbing properties of these oligomers could change the optical properties of aerosols and as such influence the earth's radiation budget (Rincon et al., 2009; Sareen et al., 2010), while their hydrophilic properties could increase their capacity to act as cloud condensation nuclei (Novakov and Penner, 1993; Andracchio et al., 2002; Kerminen et al., 2005).

3.3 Structural elucidation of the oligomers

Since accretion reactions of MGly under cloud conditions follow both mechanisms (i.e., aldol condensation and hydration/acetal formation), an effort was done in the present study to characterize the reaction products at the molecular level. We found that slight variations in reaction conditions (particularly the pH value) can activate different types of oligomerization mechanisms. In this respect, computational data by Krizner et al. (2009) also show that the product distribution (aldol condensates, dioxolane ring products, or even just the monomeric species of methylglyoxal) is highly sensitive to reaction conditions. Therefore, in the present study, the products were analyzed for reactions occurring in different pH ranges. At higher pH values (i.e., pH = 4–5) accretion reactions via aldol condensation took place, while those via hydration/acetal formation followed by acid-catalyzed oligomerization could not be detected. Upon decrease of the pH below 3.5 oligomerization via hydration/acetal formation became predominant.

3.3.1 Interpretation of (+)ESI mass spectral data

When samples from reactions at higher pH values (4–5) were analyzed, two distinct Gaussian distributions of peaks were observed in the positive ion mode; a first one in the m/z range 100–500 and a second one in the m/z range 500–800 (Fig. 1). A regular pattern with mass differences of 72 units between major peaks was noticed, consistent with an oligomer series. Ions in the first Gaussian distribution were observed at m/z 159, 231, 271, 303, 329, 343, 375, 383, 401, 447, and 487, while ions in the second one were detected at m/z 519, 527, 559, 583, 599, 617, 635, 655, 671, and 727. The MS^n fragmentation behavior of major ions at m/z 271, 303, 375, and 447 indicates the presence of hemiacetal groups. Two successive neutral losses of methanol (32 u) were observed, consistent with two hemiacetal groups. The formation of the double hemiacetal can be explained by addition of methanol (i.e., the solvent used in ESI to dilute the sample) to the carbonyl functions. Following the loss of two molecules of methanol, there was a unique loss of the monomeric unit (72 u). The major ions at m/z 583, 655, and 727 in the second Gaussian distribution showed four successive losses of methanol followed by a loss of 72 u. Hence, oligomer molecules with four hemiacetal groups were identified in addition to oligomers containing two hemiacetal groups (i.e., at m/z 591, 559, 519, and 487). The presence of four hemiacetal groups was not observed for the lower-MW oligomers.

Table 1. Proposed ion structures attributed to selected aldol condensation products of methylglyoxal on the basis of interpretation of ESI mass spectral data and mechanistic considerations (Scheme 2).

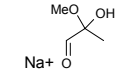
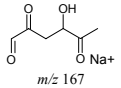
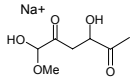
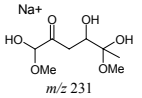
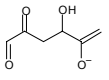
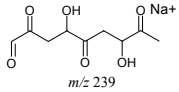
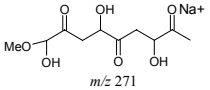
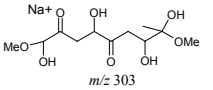
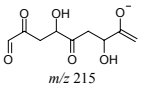
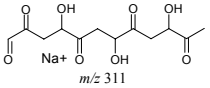
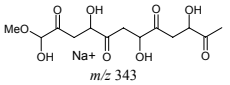
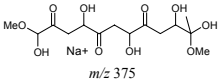
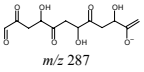
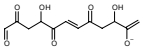
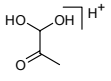
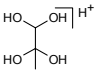
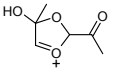
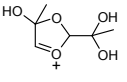
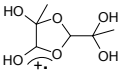
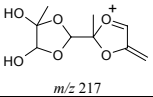
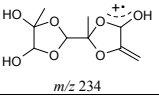
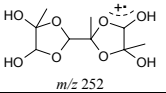
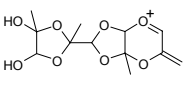
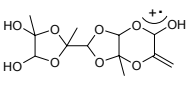
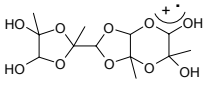
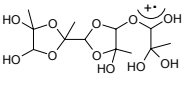
	Positive mode			Negative mode
monomer	 *m/z* 95	 *m/z* 127	 *m/z* 159	not observed
2-mer	 *m/z* 167	 *m/z* 199	 *m/z* 231	 *m/z* 143
3-mer	 *m/z* 239	 *m/z* 271	 *m/z* 303	 *m/z* 215
4-mer	 *m/z* 311	 *m/z* 343	 *m/z* 375	 *m/z* 287  *m/z* 269

Table 2. Proposed ion structures attributed to selected hydration/acetal products of methylglyoxal on the basis of interpretation of (+)ESI mass spectral data and mechanistic considerations (Scheme 1).

monomer	 *m/z* 73	 *m/z* 91	 *m/z* 109	
2-mer	 *m/z* 145	 *m/z* 163	 *m/z* 180	
3-mer	 *m/z* 217	 *m/z* 234	 *m/z* 252	
4-mer	 *m/z* 289	 *m/z* 306	 *m/z* 324	 *m/z* 342

The second most abundant ion series in the first Gaussian distribution (i.e., at m/z 203, 275, 347, 419, and 491) and the second one (i.e., at m/z 635, 617, 689) were identified as oligomers containing two hydroxyl groups because they resulted in two successive losses of H_2O (18 u). After loss of two molecules of H_2O, a loss of the monomeric unit (72 u) was noted. Figure 3 illustrates MS^2 product ion spectra of protonated oligomer molecules containing four monomer units ($n = 4$) and terminal hemiacetal or gem-diol functions, along with a set of MS^2product ion spectra corresponding to the protonated basic oligomer series containing terminal keto groups with n between 4 and 8. The fragmentations observed in the three oligomer series are summarized in Fig. 4.

The first oligomer series (white circles) comprises products formed by self-oligomerization of MGly via aldol condensation. The ion with the lowest m/z value of the white series corresponds to sodiated MGly $[MGly+Na]^+$ (m/z 95), formed by cationization of MGly with Na^+ present in the electrospray ion source. The mass increases of 72 u, leading to ions at m/z 167, 239, and 311, are consistent with addition of β-hydroxy ketone ($C_3H_4O_2$, enol form) units via the aldol condensation mechanism. The oligomer pattern could be followed until m/z 599, corresponding to the aldol product ion $[8MGly + Na]^+$. Beyond m/z 600, the spectra became too crowded, making assignment of ion structures difficult. Selected tentative structures based on mass

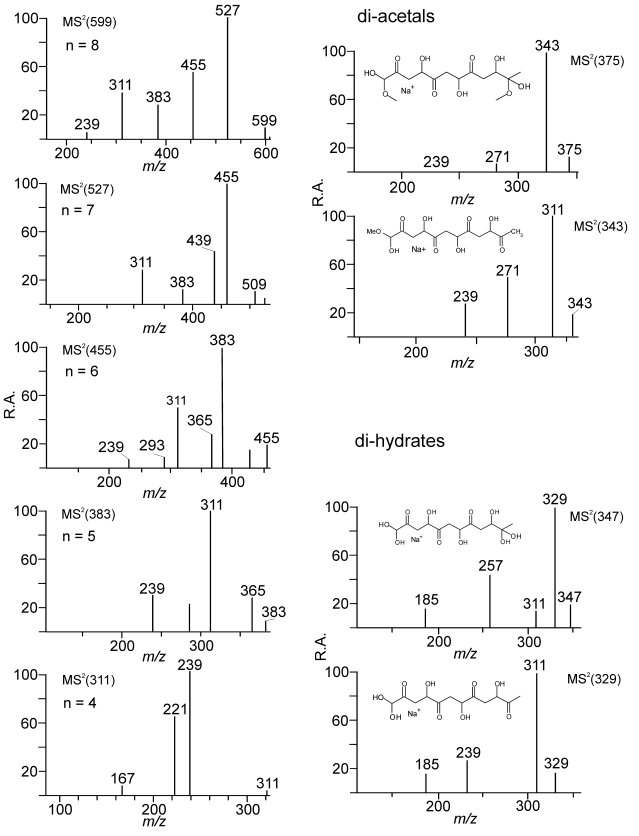


Fig. 3. MS^2 product ion spectra for ions formed in (+)ESI-MS of a series of oligomers (n = 4-8), and corresponding acetals and hydrates obtained from the reaction mixture of MGly (10^{-3} mol L^{-1}) with ammonium sulfate (10^{-4} mol L^{-1}) at pH = 4.5 and T = 15 °C after one hour reaction.

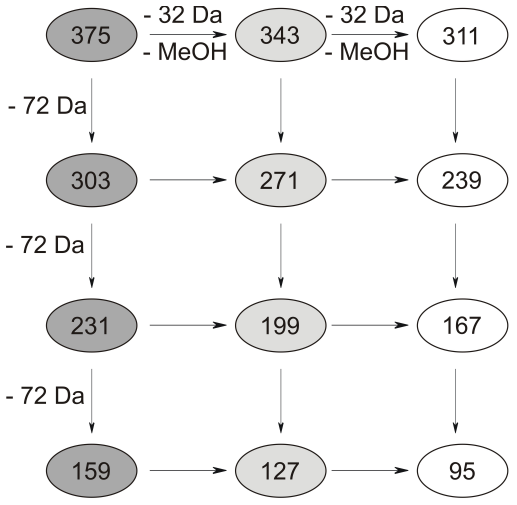


Fig. 4. Fragmentation sequence for the three oligomer series observed in ESI-MS (positive mode) from the reaction mixture of MGly (10^{-3} mol L^{-1}) with ammonium sulfate (10^{-4} mol L^{-1}) at pH = 4.5 and T = 15 °C after one hour reaction.

spectral interpretation for the oligomer series up to n = 4 and mechanistic considerations (Scheme 2) are presented in Table 1. Additional tentative structures are given in Table S2 of the supplement, http://www.atmos-chem-phys.net/10/3803/2010/acp-10-3803-2010-supplement.pdf. No evidence was found for structures formed through the first oligomerization mechanism (five-membered ring systems) at the higher pH values.

Upon decrease of the pH to a value $\leq$3.5 oligomerization via the acetal/hemiacetal mechanism became predominant. An oligomer series could be discerned with distinct ions at m/z 180, 234, 252, 270, 306, 324, 342, 396, 486, 594, 666, 738, and 810 (Fig. 2). Abundant ions are present at m/z 234, 252, 270, 306, 324, and 342, corresponding to major species of the oligomer series. Selected tentative structures up to the n = 4 oligomer series based on mass spectral interpretation and mechanistic considerations (Scheme 1) are presented in Table 2. Additional tentative structures are given in Table S2 of the supplement. The ions at m/z 217, 234, and 252 are assigned to trimer species, while the ions at m/z 289, 306, 324, and 342 are attributed to tetramer species. The remaining abundant ion at m/z 272 can be explained by loss of the monomeric unit (72 u) from the m/z 342 tetramer species. An intriguing observation is that these oligomers are detected in (+)ESI as molecular radical cations and not as protonated molecules. A possible explanation for this phenomenon is that molecular radical cations are produced from easily oxidizable compounds through an electrochemical oxidation process that is inherent to (+)ESI (Blades et al., 1991; Vessecchi et al., 2007). Figure 5 shows MS^2 and MS^3 product ion spectra for the tetrameric species detected at m/z 342; the fragmentation pathways support the proposed ion structure.

3.4 Interpretation of (−)ESI mass spectral data

To further support the identification of the oligomer series proposed above, negative mode analysis was also performed for the two reaction mixtures in both pH ranges (i.e., pH = 3–4 and 4–5). For oligomers produced by aldol condensation, deprotonated molecules of the first Gaussian distribution in addition to deprotonated crotonization products were observed (Fig. 6). The formation of deprotonated molecules can be explained by proton abstraction from mildly acidic protons that are available in aldol oligomers. Indeed, each oligomer formed by aldol condensation contains a terminal methyl ketone part that can tautomerize to an enol group from which a proton can be abstracted (Table 1). Major ions with a regular mass difference of 72 u are seen at m/z 143, 215, 287, 359, and 431, corresponding to those observed in the positive mode. Figure 6 shows MS^2 and MS^3 product ion spectra for the m/z 215 species; the observed fragmentation supports the proposed ion structure. The ions at m/z 269, 341, and 413 correspond to the dehydrated forms of

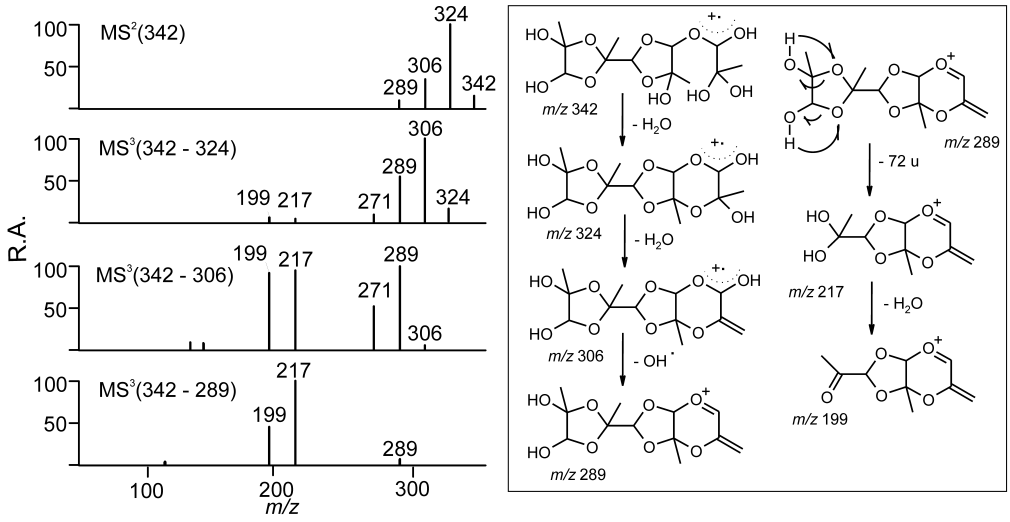


Fig. 5. MS^2 and MS^3 product ion spectra obtained for one of the major acetal ions (m/z 342) present in the (+)ESI mass spectrum obtained from the reaction mixture of MGly with ammonium sulfate at pH = 3.2 and T = 15 °C after one hour reaction, and fragmentation pathways supporting the proposed m/z 342 ion structure.

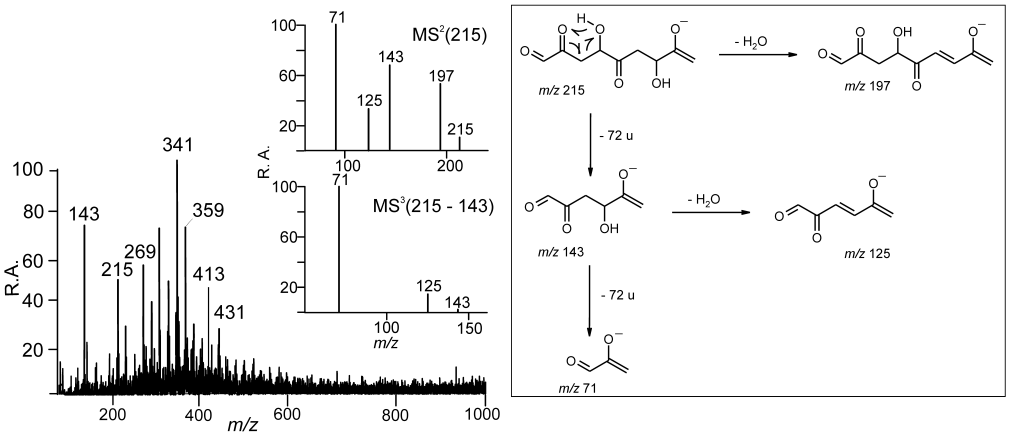


Fig. 6. ESI mass spectrum (negative mode) obtained from the reaction mixture of MGly (10^{-3} mol L^{-1}) with ammonium sulfate (10^{-4} mol L^{-1}) at pH = 4.5 and T = 15 °C after one hour reaction, MS^2 and MS^3 product ion spectra for the oligomer species detected at m/z 215, and fragmentation pathways supporting the proposed m/z 215 ion structure.

the species detected at m/z 287, 359, and 431, respectively; these ions may be due to the crotonized forms or may correspond to fragment ions formed by loss of water through an energetically favorable rearrangement reaction as shown in Fig. 6 for the m/z 215 species.

Deprotonated molecules of five-membered ring oligomers formed by acetal reactions were not observed in the negative ion mode. This could be explained by the electron-releasing nature of adjacent methyl groups hindering the ionization of hydroxyl groups. Furthermore, no evidence was found for organosulfate formation in aqueous solutions simulating a cloud medium. Organosulfates were detected previously in chamber studies where gaseous dicarbonyls from the photooxidation of isoprene in the presence of acidic ammonium sulfate seed aerosol were reactively taken up in the particle phase and sulfated (Liggio et al., 2005a; Surratt et al., 2007). Organosulfates would produce deprotonated molecules in (−)ESI-MS at a m/z value equal to (M + 97) and characteristic product ions (i.e., the bisulfate anion at m/z 97 $[HSO_4]^-$ and the radical anion at m/z 80 $[SO_3]^-$). The lack of organosulfate formation in aqueous solutions simulating dark cloud reactions is in agreement with results obtained in a recent study by Galloway et al. (2009) on organosulfate formation from glyoxal, which demonstrated that in addition to reactive uptake irradiated conditions (or photochemistry) are required for the formation of organosulfates.

4 Atmospheric implications

Based on interpretation of ESI-MS data obtained in the positive and negative ionization modes, the structures of major oligomers formed by aldol condensation and hydrate/acetal formation from methylglyoxal have been tentatively identified (Tables 1 and 2). Slight variations in reaction conditions (particularly the pH value) were found to activate different oligomerization mechanisms, consistent with the computational study by Krizner et al. (2009). In cloud conditions, the self-oligomerization of methylglyoxal occurs preferentially via aldol condensation instead of hydrate/acetal formation and is favored at higher pH. Thus, in areas where acid seed aerosols are present in high concentrations, the hydrate/acetal formation mechanism is expected to be important, and the pH is probably a limiting factor for it in clouds. This result is also consistent with theoretical calculations carried out by Barsanti and Pankow (2005), which indicated that aldol condensation is thermodynamically favorable for methylglyoxal at atmospheric concentrations. With respect to aldol condensation under acidic conditions, our results are also in agreement with the study by Nozière and Esteve (2007), who provided evidence for formation of aldol condensation products from a series of carbonyl compounds other than methylglyoxal in strong acidic media (96–75 wt% H_2SO_4). More recently, Sareen et al. (2010) reported aldol condensation products from methylglyoxal by NH_4^+-catalyzed reactions, while De Haan et al. (2009) reported pyruvic acid-catalyzed oligomerization from methylglyoxal. The aldol products found in the latter investigations were not detected in the present study, probably because of milder reaction conditions.

We demonstrate for the first time that acid-catalyzed self-oligomerization of methylglyoxal via aldol condensation reactions takes place under dark cloud conditions. Furthermore, we show that oligomerization is not only catalyzed by ammoniumsulfate but rather depends on the ionic strength and the acidity of the medium. Although formation of aldol products is kinetically favorable, the process does not appear to occur in the presence of light when OH radicals are present (Altieri et al., 2008). It is therefore proposed here that aldol and acetal oligomer formation could be an important process during nighttime that contributes to SOA production. Further research on the stability of aldol and acetal oligomers and the effect of different parameters (i.e., pH, ionic strength, and ionic composition) on their formation is in progress.

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